

High Resolution Infrared Spectroscopy in Doped Parahydrogen (pH₂) Solids: CO/pH₂ -- a Molecular Thermometer

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The phenomenon of high resolution ($\Delta\nu/\nu \sim 10^{-6}$) infrared (IR) matrix isolation spectroscopy in cryogenic parahydrogen (pH₂) solids was first demonstrated by Oka and co-workers at the U. of Chicago [1], and subsequently extended to more general dopant species in collaboration with Momose, Shida and co-workers at Kyoto U. [2]. Both groups prepare doped pH₂ solids by condensing gas mixtures in an enclosed cell at $T \approx 8$ K, producing centimeters-thick, beautifully transparent, hexagonal-close-packed (hcp) polycrystalline solids. To date, concentrations of chemically interesting dopants isolated by this method have been limited to below ~ 1 PPM.

We have developed an alternative doped solid pH₂ preparation technique based on rapid vapor deposition of precooled pH₂ gas onto a substrate-in-vacuum at $T \approx 2$ K [3,4]. The resulting millimeters-thick samples are remarkably transparent, even capable of escaping casual visual detection; in sharp contrast to previously described "completely opaque brown-black" vapor deposited hydrogen solids [5]. Our co-deposition geometry enables us to trap dopant species produced by a wide variety of methods, with excellent isolation efficiencies even at dopant concentrations exceeding 100 PPM. The excellent optical properties of our samples permit their spectroscopic interrogation at wavelengths from the vacuum ultraviolet to the mid-IR. The long useful pathlengths enable the detection of low concentration or weakly absorbing species.

A recent collaborative study comparing the spectroscopy of CH₄ doped pH₂ solids produced by the two sample preparation methods demonstrated the suitability of the rapid vapor deposited solids as hosts for high resolution IR absorption spectroscopy [6], and confirmed our previous determination of a mixed face-centered-cubic (fcc) and hcp polycrystalline structure for the as-deposited solids [3]. Annealing of these samples to $T \approx 5$ K results in the nearly complete and irreversible conversion of the fcc regions to hcp. In contrast, spectra of C₆₀ doped pH₂ solids indicate that similar temperature cycling of these samples does not eliminate the fcc regions [7]. We conjecture that the multi-substitutional sites occupied by the large C₆₀ dopant molecules intrude into adjacent close-packed planes, precluding their relative slipping motion and thus the fcc to hcp conversion process.

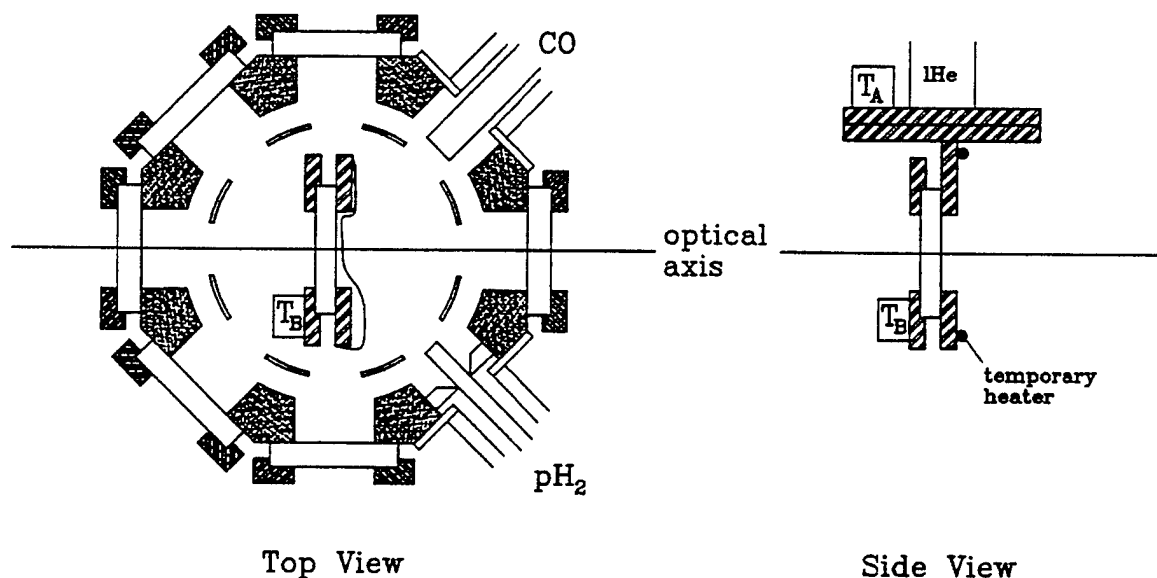
While we are making steady progress in applying spectroscopic techniques to determine the microscopic structures of our doped rapid vapor deposited samples, we have only recently begun our efforts to understand their bulk (e.g. mechanical strength, thermal transport) properties. We note that our apparatus is configured to facilitate sample production and optical access, as shown in the Figure. The attendant numerous openings in the liquid nitrogen cooled radiation shield result in radiative heat loads on the sample which are difficult to quantify. Despite this limitation, we have performed a series of spectroscopic experiments designed to probe bulk temperature changes in the pH₂ solids during the rapid vapor deposition process.

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We utilize reversible temperature dependent changes in the IR absorption spectrum of CO molecules isolated in solid pH_2 as a "molecular thermometer." High-resolution spectra are not required for this technique; an instrumental resolution of $\approx 1 \text{ cm}^{-1}$ FWHM is optimum. The advantage of such a thermometer is that the rotational degrees of freedom of the CO molecules are certain to be in thermal equilibrium with the pH_2 solid; the difficulties come in obtaining an accurate absolute calibration.

The intensity of an isolated absorption feature near 2135 cm^{-1} shows a monotonic increase with temperature over the 2 to 5 K range. We estimate that the thermally populated initial state of this transition is $\approx 8 \text{ K}$ above the ground state of CO/ pH_2 . During the deposition of $\approx 100 \text{ PPM}$ CO/ pH_2 samples, we detect temperature gradients $\sim 10 \text{ K/cm}$ in $\sim 0.1 \text{ cm}$ -thick samples subjected to heat loads $\sim 10 \text{ mW/cm}^2$. The resulting estimated thermal conductivity is $2(\pm 1) \text{ mW/cm-K}$, averaged over the 2 to 5 K region. This value is about three orders of magnitude lower than the thermal conductivity of single crystal solid pH_2 , and more than an order of magnitude lower than previously measured for pH_2 solids doped with 100 PPM concentrations of heavy impurities [8]. We attribute this abnormally low thermal conductivity to the previously determined mixed hcp/fcc structure of the rapid vapor deposited solids.



Experimental Schematic

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